Limited dechlorination of sea-salt aerosols during the last glacial period: Evidence from the European Project for Ice Coring in Antarctica (EPICA) Dome C ice core

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[1] Chloride (Cl^-) and sodium (Na^+) in ice cores originate mainly from sea salt, and one would thus expect the Cl^-/Na^+ ratio to reflect the seawater ratio. However, at Dome C, a low-accumulation site in East Antarctica, this is not the case in present-day snow. Instead, a Cl^- excess relative to Na^+ is observed in surface snow, and within a few meters depth the Cl^- concentration decreases, and the Cl^-/Na^+ ratio becomes significantly lower than the seawater ratio. Aerosol studies at coastal Antarctic sites have shown that the reaction of sea-salt aerosols with nitric and sulphuric acid leads to the formation of HCl that eventually escapes the sea-salt aerosol. The observed decrease in Cl^- concentrations in the uppermost snow layers is due to reemission of HCl from the snow. Postdepositional loss of HCl depends among other factors on the accumulation rate at the site, with lower accumulation rates leading to larger losses. During the Last Glacial Maximum (LGM) the Cl^-/Na^+ ratio is relatively stable and close to the seawater ratio, despite the even lower accumulation rate during that time. The likely explanation for this conflicting observation is that high levels of dust neutralized nitric and sulphuric acids during the LGM which in turn reduced the formation of HCl from sea-salt aerosol. With less or no HCl formed, postdepositional loss would be prevented, keeping the Cl^-/Na^+ ratio close to that of sea water. *INDEX TERMS:* 0368 Atmospheric Composition and Structure: Troposphere—constituent transport and chemistry; 0305 Atmospheric Composition and Structure: Aerosols and particles (0345, 4801); 1615 Global Change: Biogeochemical processes (4805); 3344 Meteorology and Atmospheric Dynamics: Paleoclimatology; 9310 Information Related to Geographic Region: Antarctica; *KEYWORDS:* sea-salt aerosol, ice core records, Antarctica

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1. Introduction

[2] Ice cores offer a unique possibility to reconstruct variations of past atmospheric aerosol concentrations, transport and transformation during transport. Cl^- and Na^+ have been used as indicators of sea-salt aerosols, as they are the main constituents of sea salt and are routinely analyzed in chemical ice core analysis. Usually, sea-salt aerosol is believed to originate from open water and it was assumed that sea ice extent would influence the source area in the vicinity of the Antarctic continent. More recently, evidence for an additional sea-salt aerosol source, particularly in winter, has been presented [*Wagenbach et al.*, 1998]. On the basis of the chemical signature of atmospheric aerosols, back trajectory calculations and satellite imagery, *Rankin et al.* [2002] showed that frost flowers, which form from the brine on new sea ice, are the dominant contributors to coastal Antarctic sea-salt aerosol. Sea-salt aerosols from frost flowers are slightly depleted in Na^+, but this depletion is limited to approximately 10%. So whether the sea-salt aerosol is produced over open water or fresh sea ice, one would expect a Cl^-/Na^+ ratio close to the one found in seawater.

[3] Other sources than sea salt are known to contribute to the Na^+ and Cl^- concentrations of polar snow, which could potentially change the Cl^-/Na^+ ratio in snow and ice

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compared to the ratio found in seawater. Some Na^+ and a negligible amount of Cl^- comes along with mineral dust. Our analytical method only accounts for the soluble fractions, i.e., dust is unlikely to contribute to the Na^+ concentrations measured. However, there remains some uncertainty due to insufficient knowledge of the availability of Na^+ from minerals. Nevertheless, even if all Na^+ of the mineral dust would be dissolved during analysis, the terrestrial contribution to Na^+ at Dome C would be below 10% during the Holocene and below 25% in the Last Glacial Maximum (LGM) (based on an average crustal Ca^{2+}/Na^+ ratio of 1.78 [*Bowen*, 1979]). For Cl^-, an additional source is HCl of volcanic origin. Such emissions are easily identified as they are fairly episodic and normally coincide with prominent SO_4^{2-} peaks.

[4] Past studies presenting Na^+ and Cl^- concentrations in Antarctic snow and ice have shown that the Cl^-/Na^+ ratio is very different from the seawater ratio [*Legrand et al.*, 1988; *Legrand and Delmas*, 1988a] with values at a single site sometimes being higher and sometimes lower than in seawater. A mechanism based on the reaction of sea-salt aerosol with acids leading to the formation of HCl has been proposed [*Legrand and Delmas*, 1988b]. Postdepositional HCl losses in surface snow have been observed on the East Antarctic plateau [*Wagnon et al.*, 1999], resulting in Cl^-/Na^+ ratios below the seawater ratio at a few meters depth. During the last glacial period, these losses seem less pronounced or absent, which has been assigned to shorter atmospheric residence times of the sea-salt aerosol [*Legrand and Delmas*, 1988b] allowing for less formation of HCl. However, there is no evidence for significantly shorter transport times during the last glacial period [*Lunt and Valdes*, 2001; *Krinner and Genthon*, 2003], and a recent study of dust particle sizes even tended to longer atmospheric residence times of the particles deposited at Dome C during the LGM [*Delmonte et al.*, 2002]. Thus no consistent explanation for the variation of the Cl^-/Na^+ ratio has been found so far.

[5] The present work identifies the mechanisms leading to changes in the Cl^-/Na^+ ratio preserved in Antarctic ice cores and describes the changing interplay of these factors over glacial-interglacial cycles. In order to explain the various determining factors, we use the new record from Dome C (75°06′S, 123°24′E) back to 45 kyr B.P. This section has been drilled and analyzed in the framework of the European Project for Ice Coring in Antarctica (EPICA) from 1996 to 1999.

2. Methods

[6] The chemical analysis of the ice core from Dome C was done by continuous flow analysis (CFA) for Na^+ and Ca^{2+} [*Röthlisberger et al.*, 2000a], fast ion chromatography (FIC) for Cl^- and SO_4^{2-} [*Udisti et al.*, 2000] and standard ion chromatography (IC) for all major ions [*Littot et al.*, 2002]. CFA and FIC were done in the field during the core processing campaigns. These two methods are based on a continuous sample obtained by melting a subsection of the ice core on a melter where the outer, possibly contaminated part of the sample, is discarded. CFA uses spectrophotometric methods for the determination of Na^+ and Ca^{2+} which produce data at a spatial resolution of the order of 1 cm (i.e., 0.35 yr during the Holocene and 0.9 yr during the LGM). FIC takes one sample every minute which is then analyzed by ion chromatography, which results in a spatial resolution of approximately 4 cm. IC analysis on discrete samples was done in five European laboratories after retrograding of the core. Detailed description of the methods can be found in the references cited above. Generally, we used 55-cm averages of the high-resolution records.

[7] In this study, we present Cl^- and Na^+ data from the IC analysis of discrete samples in order to compare Cl^- and Na^+ data that were measured on exactly the same sample. However, using CFA or FIC data leads to the same conclusions. The Ca^{2+} record shown was measured by CFA. The advantage of one method over the other and the agreement between the methods used is discussed in detail by *Littot et al.* [2002].

[8] On the basis of the sulphate record [*Udisti et al.*, 2000], we identified sections with volcanic input and checked for indication of significant amounts of Cl^- of volcanic origin. However, there were few events that showed markedly elevated Cl^- concentrations and the impact on the 55-cm averages was negligible. Therefore, we did not correct the record for potential volcanic Cl^-.

3. Observations

[9] The detailed Cl^- and Na^+ records from Dome C showed several different regimes with respect to the Cl^-/Na^+ ratio. At the snow surface, a considerable surplus of Cl^- relative to Na^+ is observed (Figure 1). However, in the first few meters, the Cl^- concentrations decrease steadily and at about 4 m depth, a Cl^- deficit relative to Na^+ is observed. This deficit is maintained throughout most of the Holocene, except for the time period between 8.8 and 11.3 kyr B.P. (Figure 2), where some excess Cl^- is observed. The excess during this early Holocene period is smaller than the excess found at the surface, but still remarkably high considering the rest of the Holocene. During the Last Glacial Maximum (18 to 24 kyr B.P.) the Cl^-/Na^+ ratio was rather constant and close to the ratio observed in seawater [*Bowen*, 1979]. In contrast to that, the Cl^-/Na^+ ratio showed large fluctuations in the earlier glacial period (35 to 45 kyr B.P.). Similar to the Cl^- concentrations also the nss-Ca^{2+} (nss$-Ca^{2+} = Ca_{tot}^{2+} - 0.038 * Na^+$) concentrations changed dramatically during this period, while the Na^+ concentrations were relatively stable. During the Eemian, the previous warm period, excess Cl^- was found in the Vostok ice core [*Legrand et al.*, 1988], contrasting the distinct Cl^- deficit observed during most of the Holocene in Vostok as well as in Dome C.

4. Discussion

[10] In the following sections, we discuss the main phenomena of the Cl^-/Na^+ ratio of the Dome C record, namely the observed Cl^- excess in surface snow and in the early Holocene, the depletion of Cl^- in the uppermost meters of the snowpack, and the stable Cl^-/Na^+ ratio close to the seawater ratio during the LGM. The factors responsible for these three aspects allow a consistent explanation of the Cl^-/Na^+ ratio observed in Antarctic ice cores.

4.1. Surface Excess of Cl^-

[11] Several studies have emerged lately showing considerable Cl^- depletion of sea-salt aerosols in coastal Antarctica during the summer months [*Kerminen et al.*, 2000; *Wagenbach et al.*, 1998]. Similar results have been

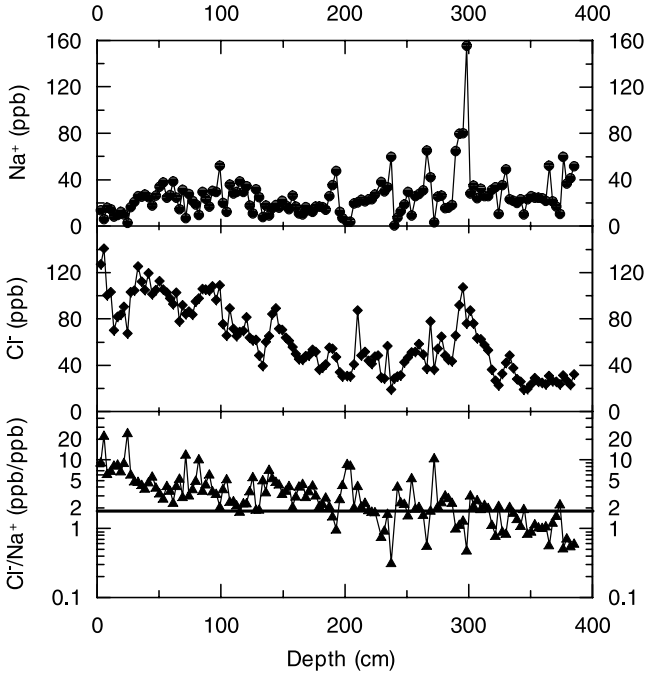

Figure 1. Cl^- and Na^+ concentrations and Cl^-/Na^+ ratio in the top 4 m of snow at Dome C, Antarctica. The thick horizontal line in the bottom graph reflects the Cl^-/Na^+ ratio in seawater. See color version of this figure in the HTML.

reported for South Pole summer aerosols [*Arimoto et al.*, 2001]. Recently, these findings have been confirmed in the context of a comprehensive, year-round aerosol monitoring campaign at the French station Dumont d'Urville, coastal Antarctica [*Jourdain and Legrand*, 2002]. The depletion during summer ranged from 10% to 90%, depending on the total sea-salt aerosol load and the aerosol size. On the basis of size-segregated analyses of the aerosols, HNO_3 accounted for some if not for most of the dechlorination of the aerosol [*Jourdain and Legrand*, 2002; *Kerminen et al.*, 2000] and sulphur species, mainly H_2SO_4, for the remainder. Dechlorination can likely occur both during transport and in the snowpack after deposition. This would then allow dechlorination even of sea salt deposited in winter, when atmospheric acidity in the coastal regions is low.

[12] The product of this dechlorination, HCl, has been measured in the atmosphere at Dumont d'Urville during a year-round monitoring campaign [*Jourdain and Legrand*, 2002]. It showed highest atmospheric HCl levels in summer, when dechlorination of the aerosol is most pronounced. The HCl concentrations matched the observed losses fairly well, with HCl only slightly exceeding the Cl^- deficit in the aerosol, which was attributed to a slightly longer atmospheric lifetime of HCl compared to sea-salt aerosol.

[13] This difference in atmospheric lifetime could partly explain the excess Cl^- observed in surface snow at inland Antarctic sites. While the sea-salt concentrations in snow drop rapidly with distance from the coast, the concentrations of sulphate, which is related to smaller aerosols, decrease more slowly [*Minikin et al.*, 1994]. HCl is either in the gas phase or associated to a smaller aerosol mode than Na^+ and most likely behaves similar to sulphur species, i.e., due to the longer atmospheric lifetime being transported more easily over long time periods. This results in the tendency to higher Cl^-/Na^+ ratios at sites further on the Antarctic plateau (Figure 3). The longer the transport route, the more transport favors Cl^- over coarse sea-salt particles and relatively more excess Cl^- arrives at the site.

[14] During winter however, no dechlorination of the sea-salt aerosol is observed at coastal Antarctica [*Jourdain and Legrand*, 2002]. On the contrary, a slight excess of Cl^- was observed arising from sea-salt aerosol produced from frost flowers. *Wagenbach et al.* [1998] reported a Na^+ depletion in winter aerosol at coastal Antarctica of up to 10%, which would contribute to the Cl^- excess at inland sites.

4.2. Postdepositional Loss of HCl

[15] As a result of the processes described, what is transported inland is sea-salt aerosol that is partly dechlorinated, along with HCl in the gas phase or on smaller aerosols. However, it has been shown that HCl is reversibly deposited to the snow surface: Although excess Cl^- is found in surface snow, part of it is released back into the boundary layer atmosphere. At some sites (e.g., Vostok [*Wagnon et al.*, 1999], Dome C (Figure 1)), this leads gradually to Cl^-/Na^+ ratios below the seawater ratio at a few meters depth, i.e., most of the initially deposited HCl has been reemitted and no longer balances the Cl^- deficit in sea-salt aerosol. Cl^-/Na^+ ratios below the seawater ratio are sustained during most of the Holocene (Figure 2, or for Vostok see [*Legrand et al.*, 1988]).

[16] Detailed investigations of postdepositional effects on other reversibly deposited substances (formaldehyde (HCHO) and hydrogen peroxide (H_2O_2)) have shown that apart from temperature also accumulation rate is a crucial factor for preservation in snow [*Hutterli et al.*, 2003]. There is a critical accumulation rate, below which most or all of the excess substance is released into the atmosphere again. Although the quantitative knowledge of the postdepositional processes affecting Cl^- is less advanced than for HCHO and H_2O_2, Cl^- profiles from other Antarctic sites indicate that the postdepositional losses are most pronounced at sites with accumulation rates below 4 g cm^{-2} yr^{-1} (see data archived at the National Snow and Ice Data Center, http://www.nsidc.org). At South Pole, for example, where the accumulation rate is estimated to be around 8 g cm^{-2} yr^{-1}, the Cl^-/Na^+ ratio does not drop below 1.8 [*Whitlow et al.*, 1992].

[17] Comparing the Dome C Holocene Cl^-/Na^+ record with the accumulation rate supports the hypothesis of accumulation rate dependent preservation of Cl^- (Figure 2). The accumulation rate [*Schwander et al.*, 2001], which has been derived from the deuterium record δD, was elevated during the early Holocene, approaching the estimated critical accumulation rate for the preservation of Cl^- of 4 g cm^{-2} yr^{-1}. During this period, the Cl^-/Na^+ ratio was again higher than the sea water ratio but considerably lower than in the uppermost snow layers (Figure 1), i.e., some HCl probably still escaped the snowpack after deposition. But HCl losses were reduced compared to the more recent Holocene due to the increased accumulation rate that preserved some excess Cl^-. This effect also explains the observed Cl^- excess in the Vostok record of the Eemian: The accumulation rate was higher during the Eemian than during the Holocene (above 3 g cm^{-2} yr^{-1}, F. Parrenin, personal communication, 2002), leading to better preservation of Cl^- in the snow.

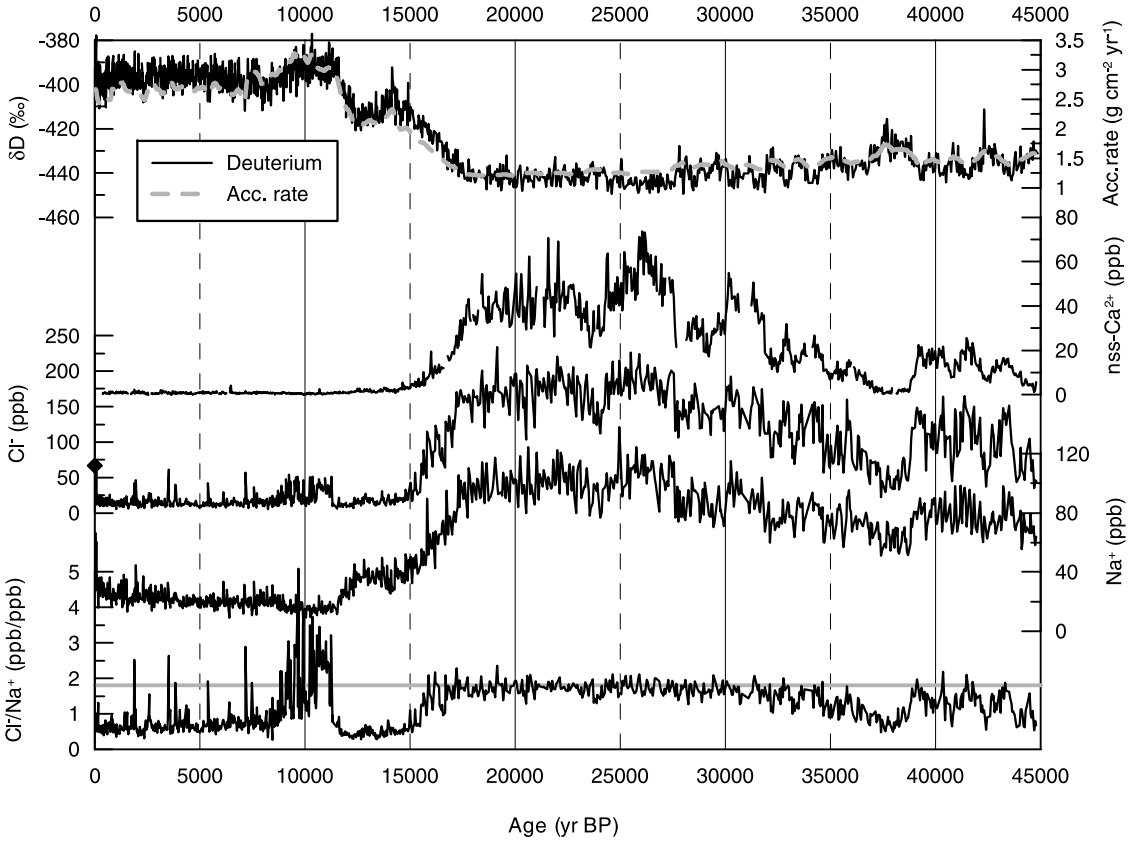

Figure 2. Cl^-/Na^+, Na^+, Cl^- and nss-Ca^{2+} records covering the past 45 kyr B.P. at 55 cm resolution together with δD [*Jouzel et al.*, 2001] and accumulation rate (yellow) [*Schwander et al.*, 2001]. The thick horizontal line in the bottom graph reflects the Cl^-/Na^+ ratio in seawater. The blue diamond on the left hand y axis corresponds to the Cl^-/Na^+ ratio averaged over the top 55 cm of the pit. See color version of figure in the HTML.

[18] In Figure 4a, the relationship between the Cl^-/Na^+ ratio and the accumulation rate is shown. The lowest Cl^-/Na^+ ratio is observed during the Antarctic Cold Reversal (ACR), and with increasing accumulation rate, the Cl^-/Na^+ ratio increased as well. However, the fact that the Cl^-/Na^+ ratio was higher during the glacial period than during the ACR despite even lower accumulation rates seems inconsistent with the postulated relationship between Cl^-/Na^+ and accumulation rate and is discussed in the following section.

4.3. Limited HCl Formation Due to High Dust Levels

[19] As seen in Figures 2 and 4a, the Cl^-/Na^+ ratio was higher during the last glacial period than during the ACR and most of the recent Holocene. In the LGM the Cl^-/Na^+ ratio remained fairly stable at the level of the seawater ratio. If the reactions between sea-salt aerosols and acids in the atmosphere were still responsible for significant dechlorination of sea-salt aerosol during the LGM, it would be very unlikely to result in a Cl^-/Na^+ ratio at Dome C that is so close to the seawater ratio. We therefore suggest that the dechlorination of sea-salt aerosol was suppressed during the LGM, limiting the formation of HCl which could escape the snowpack after deposition.

[20] It has been suggested that shorter residence times reduced the reaction between sea-salt aerosol and H_2SO_4 [*Legrand and Delmas*, 1988b], but there is no indication for significant changes in residence time. The size distribution of dust particles of the LGM suggests a tendency to longer residence times during this period [*Delmonte et al.*, 2002] and current transport models give no evidence for significantly faster transport in the LGM either [*Lunt and Valdes*, 2001; *Krinner and Genthon*, 2003].

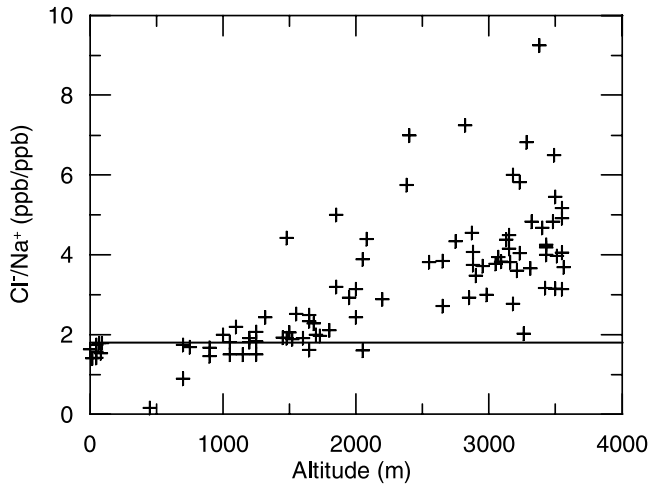

Figure 3. Cl^-/Na^+ ratio in surface snow along the 1990 International Trans-Antarctic Expedition (data from *Qin et al.* [1999]). See color version of this figure in the HTML.

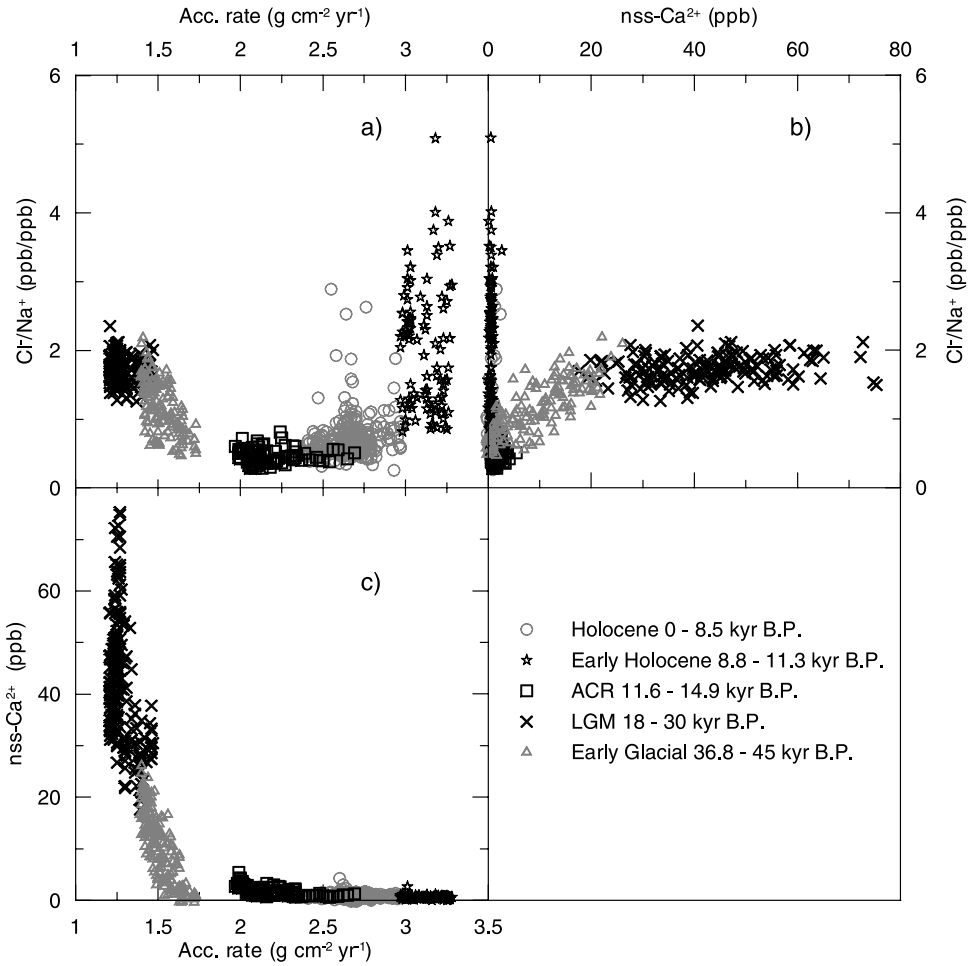

Figure 4. Relationships between the Cl^-/Na^+ ratio, accumulation rate and nss-Ca^{2+} at Dome C during different periods (55-cm averages). ACR covers the period of the Antarctic cold reversal during the transition from the LGM to the Holocene. See color version of this figure in the HTML.

[21] The Cl^-/Na^+ ratio remained close to the seawater ratio during periods with high nss-Ca^{2+} concentration (a proxy for dust) as seen in Figure 2. It is known that uptake on dust is an efficient pathway for HNO_3 removal [*Hanisch and Crowley*, 2001] and there is evidence for such reactions to have happened during the LGM in Antarctica [*Röthlisberger et al.*, 2000b]. It is conceivable that H_2SO_4 is neutralized as well, but unlike for HNO_3, this has no effect on the preservation of SO_4^{2-} in snow and can thus not be inferred from ice core records. Studies regarding the agents responsible for the dechlorination of sea salt are not yet fully conclusive: *Kerminen et al.* [2000] found that H_2SO_4 causes slightly more of the observed dechlorination than HNO_3, and that even MSA (methane sulphonic acid) contributes to some extent. *Jourdain and Legrand* [2002], on the other hand, attribute most of the dechlorination to HNO_3, with little effect of the sulphur compounds.

[22] During the LGM, the Na^+ flux at Dome C doubled, whereas the dust flux was more than 20 times higher than during the Holocene [*Röthlisberger et al.*, 2002a]. Such a high dust load could reduce the atmospheric lifetime of HNO_3 by a factor of 25 [*Röthlisberger et al.*, 2002b] and could make the effect of dechlorination caused by HNO_3 negligible. On the basis of the balance of anions and cations, we estimate that the dechlorination is equally caused by HNO_3 and H_2SO_4 under present-day conditions. By eliminating the effect of HNO_3 under glacial conditions, dechlorination would be reduced by a factor of 2. On the other hand, the SO_4^{2-} flux during the LGM was comparable to the Holocene flux [*Traversi et al.*, 2002]. Given the greatly enhanced abundance of dust relative to sea salt during the LGM, it seems likely that some of the H_2SO_4 reacted with dust which led to a further reduction in dechlorination.

[23] In Figure 4b, the relationship between the Cl^-/Na^+ ratio and nss-Ca^{2+} is shown. During the LGM, the Cl^-/Na^+ ratio is fairly constant, independent of the nss-Ca^{2+} level. It seems as if a critical atmospheric dust level to prevent significant dechlorination is reached when nss-Ca^{2+} concentrations at Dome C are around 20 ppbw. In the earlier part of the glacial period, however, dust levels drop markedly (see Figures 2 and 4c and *Röthlisberger et al.* [2002a]), leading to the formation and subsequent postdepositional loss of HCl. During the transition and the Holocene, dust levels are extremely low and have no impact on the Cl^-/Na^+ ratio.

5. Conclusions

[24] The key to understanding the Cl^-/Na^+ ratio of the Dome C ice core record lies in the formation of HCl and the subsequently partly independent transport of Cl^- and Na^+

as well as the postdepositional formation and reemission of HCl from the snow pack.

[25] We have shown that, under present-day conditions, significant excess of Cl^- over Na^+ is found at inland Antarctic sites due to the formation of gas-phase HCl and the subsequent fractionation processes during long-range transport, due to Na^+ depletion of winter sea-salt aerosol and due to redeposition of HCl that has been emitted from deeper snow layers. During the LGM the formation of HCl was strongly reduced due to high dust levels relative to sea salt that neutralized HNO_3 and H_2SO_4 to some extent. Therefore, no HCl that could be reemitted was formed and the Cl^-/Na^+ ratio at Dome C remained close to the sea water ratio. In the earlier part of the glacial period, dust levels dropped and accordingly, dechlorination of sea salt increased again, leading to the formation and postdepositional loss of HCl.

[26] At sites with very low accumulation rates, the reemission of HCl from the surface snow might contribute to the abundance of HCl at the air-snow interface. The reemission of HCl is highly dependent on the accumulation rate, apart from other factors such as for example temperature. At accumulation rates below 4 g cm^{-2} yr^{-1}, the postdepositional losses lead to a Cl^- deficit relative to Na^+ below the surface layers, as observed at Dome C during the later part of the Holocene. The strong accumulation rate dependency is most likely the reason for the increase in the Cl^-/Na^+ ratio to values above the seawater ratio during the early Holocene and the Eemian. This dependency could, if quantified, serve as an independent indicator of changes in accumulation rate within a small sensitive range. If additional substances with different accumulation sensitivities are combined, one might achieve an estimate of the accumulation rate. However, a prerequisite for this is a quantitative understanding of the postdepositional processes affecting Cl^-. For this purpose, atmospheric measurements combined with surface snow analyses at inland sites (e.g., Dome C) as well as laboratory studies are needed.

[27] **Acknowledgments.** This work is contribution 62 to the "European Project for Ice Coring in Antarctica" (EPICA), a joint ESF (European Science Foundation)/EC scientific programme, funded by the European Commission and by national contributions from Belgium, Denmark, France,Germany, Italy, Netherlands, Norway, Sweden, Switzerland and the United Kingdom. R.R. thanks the Swiss National Foundation for financial support.

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